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STAUFFER CHEMICAL COMPANY

HIGH ENERGY OXIDIZERS

CONTRACT Nonr-4019(00)

Project NR 093-035

Richmond Research Center
Richmond, California

STAUFFER CHEMICAL COMPANY
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"HIGH ENERGY OXIDIZERS"

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Project NR 093-035

ARPA No. 399-62

OFFICE OF NAVAL RESEARCH

WASHINGTON, D. C.

Quarterly Technical Summary Report

for the Period February 1, 1964 to May 1, 1964

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Summary

Using infrared spectroscopy the ionic structure of the chlorine-trifluoride complexes was proved in the solid form also. Conclusion was made concerning the structure of the ClF_2^+ cation. Investigations were started for the preparation of other complexes with anions of higher energy content.

Abstract

This is the first Quarterly Technical Summary Report of the second year on the investigation of chlorinetrifluoride complexes.

The IR spectra of gaseous and solid chlorinetrifluoride and arsenicpentafluoride were taken and compared with the spectrum of $ClF_2^+AsF_6^-$ and $KAsF_6$. A comparison between the spectra indicated the presence of AsF_6^- in the complex. Analogous results were obtained for the $ClF_2^+BF_4^-$ complex. From the absorption of the ClF_2^+ cation it was concluded that it exists in an angular form and is not linear.

The reaction of $AgNO_3$, $KClO_4$ and N_2O with chlorinetrifluoride was studied in an attempt to prepare $ClF_2^+X^-$ where X^- was expected to be NO_3^-, ClO_4^- or N_2OF^-.

An all metal vacuum line and a Teflon IR cell were designed for future work.

A paper was presented on the results of the first year's study at the ARPA Conference, Chicago.

Introduction

It was established earlier that the chlorinetrifluoride complexes are dissociated in solvents such as halogenfluorides. Low temperature infrared study was needed to determine the structure in solid form.

Discussion

Infrared spectra

TABLE I

$[ClF_2]^+[AsF_6]^-$	$KAsF_6$	ClF_3(g)	ClF_3(s)	AsF_5(g)	AsF_5(s)
405 s	413 ms			409 s	404 m
			499 m	488 w	
			508 m		
521 m		518 s			
		535 s			
558 m					
			604 vs		
			630 vs		
688 vs	685 vs	694 vs			
703 vs	705 vs	703 vs			
		713 vs			
729 vs	725 vs				725 vs
		741 s			738 vs
		761 s	765 m		
			770 w	786 vs	
				811 vs	
				818 m	814 vs
				858 w	
				866 w	
					891 w
		957 m		977 w	
		1022 m		1023 w	
					1101 vw
					1127 w
		1223 s			1201 w
1284 vw		1273 w			
1298 w					
		1451 s			
		1466 s			
		1488 s			
		1505 s			

The absorptions obtained for $ClF_2^+AsF_6^-$, $KAsF_6$, gaseous and solid ClF_3 and AsF_5 are tabulated in Table I.

It can be seen that the absorptions of the $ClF_2^+AsF_6^-$ cannot be due to those of ClF_3 or AsF_5 in either gaseous or solid form. The comparison of the spectra of $ClF_2^+AsF_6^-$ and $KAsF_6$ clearly indicates the presence of the AsF_6^- anion in the complex. Similar observations can be made in the case of the $ClF_2^+BF_4^-$ complex establishing the presence of the BF_4^- anion as it was already shown earlier by Selig and Shamir(1). Knowing that these complexes are formed from their components in a ratio of one:one, the presence of the AsF_6^- and BF_4^- anion leaves no doubt about the form of their chlorinetrifluoride part: it has to exist as a ClF_2^+ cation in solid phase also. In Table II the absorption of both complexes are given together with their assignment.

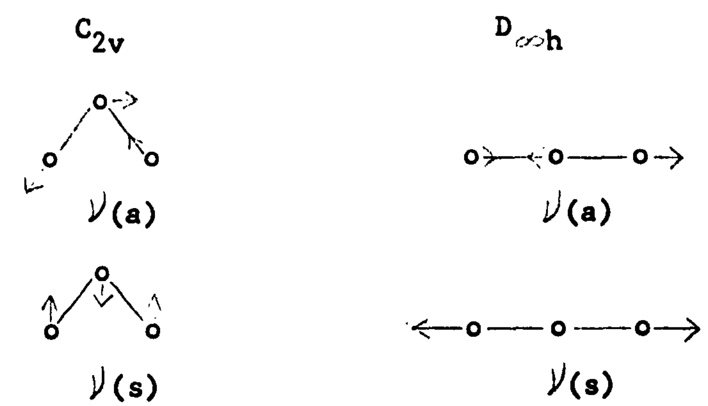
TABLE II

	$[ClF_2]^+[AsF_6]^-$	$[ClF_2]^+[BF_4]^-$
	729 cm^{-1}	1036 cm^{-1}
ν anion	703	1005
	688	
ν asClF_2^+	557	536
ν symClF_2^+	519	518

It can be seen that in each case there are two absorptions which do not belong to the anions; therefore, we must assign them to the ClF_2^+ cation. Since the highest frequency reported for a deformation vibration of the Cl-F bond is 434 cm^{-1} (2) it can be assumed that both observed absorptions are stretching modes.

Theoretically the ClF_2^+ cation could have the symmetry C_{2v} (bent form) or $D_{\infty h}$ (linear). The possible fundamentals for stretching vibrations are shown in Figure I.

FIGURE I



Since the ν(s) fundamental of symmetry $D_{\infty h}$ is IR inactive, a linear XY_2 molecule would show only one stretching vibration. Therefore, symmetry C_{2v} has to be favored, where both vibrations are IR active. Based on these results, it can be concluded that the ClF_2^+ cation has an angular form.

Reaction of ClF_3 with $AgNO_3$

This reaction was carried out in an attempt to prepare $ClF_2^+NO_3^-$ according to the following equation:

$$AgNO_3 + ClF_3 \longrightarrow ClF_2^+NO_3^- + AgF$$

The reaction, however, did not result in $ClF_2^+NO_3^-$, or if it did form during the reaction it decomposed. Silverdifluoride and NO_2F were identified as the reaction products. Based on this observation, the following equation is suggested to describe this reaction:

$$2\ AgNO_3 + 3\ ClF_3 \longrightarrow 2\ AgF_2 + 2\ NO_2F + 3\ ClF + O_2$$

Reaction between ClF_3 and $KClO_4$

The reaction which was expected to proceed in the following way:

$$KClO_4 + ClF_3 \longrightarrow KF + ClF_2^+ClO_4^-$$

did not result in any change of the $KClO_4$. X-ray analysis of the residue showed only unreacted $KClO_4$ and no KF.

Reaction between ClF_3 and N_2O

This reaction was described in a U. S. Patent as a way to prepare NF_3[3]. The reaction conditions, however, are too drastic (300°C. under pressure). It was hoped that under milder conditions the following reaction could take place:

$$N_2O + ClF_3 \longrightarrow ClF_2^+N_2OF^-$$

The N_2OF^- anion would be isoelectronic with N_2F_2 and therefore its existence might be possible. The reaction was investigated at different temperatures between -196° and 0°C., but the IR spectrum showed in each case only unreacted starting materials.

Experimental

Vacuum line

All reported reactions were carried out in a glass vacuum line.

Infrared Spectra

A Beckman IR-9 all grating instrument was used for this investigation covering a range from 400 to 4000 cm^{-1}. In addition to earlier investigations, the spectra of the complexes were taken using AgCl windows. The cell was made of glass, with an internal cold AgCl window.

Reaction between ClF_3 and $AgNO_3$

Chlorinetrifluoride was condensed on top of powdered $AgNO_3$ at -196°C. The mixture was warmed up slowly to room temperature. The gases were analyzed by IR and the presence of NO_2F was established besides unreacted chlorinetrifluoride. The dark solid residue was analyzed: Ag = 72.5%, F = 24.9%. This represents an atomic ratio of 1:1.95 between silver and fluorine. The X-ray powder diagram of the compound was also taken.

Reaction between ClF_3 and $KClO_4$

The reaction was carried in a similar way as with $AgNO_3$. The vapor phase did not contain anything outside of ClF_3 according to the IR. The white solid residue was identified by X-ray analysis as unreacted starting material.

Reaction between ClF_3 and N_2O

The two components were condensed together on the cold AgCl window of the low temperature IR cell. The IR spectrum, at temperatures between -196° and 0°C., showed only the absorptions of the starting materials. In another attempt the two components were condensed together in the vacuum line and were allowed to warm up to 0°C. No visible sign of any reaction was observed. When the liquid was warmed up to room temperature everything evaporated without any residue and the vapor phase again showed only ClF_3 and N_2O.

ls
May 21, 1964

(1) Selig H., Shamir J., Inorg. Chem. 3, 294 (1964)

(2) Classen, H. H., Weinstock, B., Malm, J. G., J. Chem. Phys. 28, 285 (1958)

(3) Marsh F., U. S. Patent 3,032,400